Claims

1. A method of sizing paper or paper board by applying a composition (A) to at least one of,

i) the surface of a formed paper or paper board sheet,

ii) a paper or paper board making cellulosic suspension prior to draining,

wherein the composition (A) comprises an aqueous dispersion of polymeric particles of particle size up to 1 micron, wherein the polymeric particles comprise a water insoluble polymer matrix, comprised of ethylenically unsaturated monomer or ethylenically unsaturated monomer blend, characterised in that an oligomer formed from a monomer blend comprising,

(a) (meth)acrylamide and

(b) an organic mercaptan or organic sulphone,

is located at the surface of the polymer particles.

2. A method according to claim 1 wherein component (b) is selected from the group consisting of C_{8-20} alkyl mercaptans, C_{5-7} cycloalkyl mercaptans, aromatic mercaptans, C_{8-20} alkyl sulphones, C_{5-7} cycloalkyl mercaptans and aromatic sulphones, preferably either dodecyl mercaptan or dodecyl sulphone.

3. A method according to claim 1 or claim 2 wherein the oligomer further comprises component (c) which is a compound of formula (1)

$CH_2=CR\text{-}Q$ (1) ,

wherein

Q is $\text{-}C(O)\text{-}Z\text{-}A\text{-}$, $\text{-}CH_2\text{-}N^+R_1R_3CH_2CR=CH_2\ X^-$ or $\text{-}CH_2\ NR_1CH_2CR=CH_2$,

Z is -O- or -NH- ,

A is $\text{-}C_nH_{2n}\text{-}B\text{-}$,

n is an integer from 1 to 4 ,

B is $-NR_1R_2$ or $-N^+R_1R_2R_3$ X^-,

R is -H or $-CH_3$,

R_1 is C_{1-4} alkyl,

R_2 is C_{1-4} alkyl,

R_3 is -H or C_{1-8} alkyl, C_{5-7} cycloalkyl or benzyl, and

X^- is an anion, preferably halide, most preferably chloride.

4. A method according to any of claims 1 to 3 wherein component (c) is dimethylaminoethyl (meth)acrylate, acid addition salt or quaternary ammonium salt thereof, preferably dimethylaminoethyl (meth)acrylate, methyl chloride quaternary ammonium salt or dimethylaminoethyl (meth)acrylate or benzyl chloride quaternary ammonium salt.

5. A method according to any of claims 1 to 4 wherein the oligomer comprises at least 85 mole % of component (a), preferably at least 90 mole %.

6. A method according to any of claims 1 to 5 wherein the oligomer comprises component (b) in an amount up to 10 mole %, preferably 2.5 - 5 mole %.

7. A method according to any of claims 1 to 6 wherein the oligomer comprises component (c) in an amount up to 10 mole %, preferably 2.5 - 5 mole %.

8. A method according to any of claims 1 to 7 wherein the oligomer further comprises component (d) which is an ethylenically unsaturated carboxylic acid or an ethylenically unsaturated carboxylic anhydride in an amount up to 10 mole %.

9. A method according to claim 8 wherein component (d) is acrylic acid or maleic anhydride and is present in an amount between 2.5 and 5 mole %.

10. A method according to any of claims 1 to 9 wherein the matrix of the polymeric particles are formed from a monomer or a monomer blend comprising monomers

selected from the group consisting of styrene, C_{1-12} alkyl (meth)acrylate, vinyl acetate and acrylonitrile.

11. A method according to any of claims 1 to 10 wherein the matrix of the polymer particles is formed from 25-75 weight %, preferably 35-65 weight %, most preferably 50 weight %, monomer or monomer blend selected from any of styrene, acrylonitrile, vinyl acetate and

C_{1-2} alkyl (meth)acrylate, preferably styrene, acrylonitrile, methyl methacrylate, methyl acrylate, ethyl methacrylate, vinyl acetate and 25-75 weight %, preferably 35-65 weight %, most preferably 50 weight %, monomer or monomer blend selected from any of C_{3-8} alkyl (meth)acrylate, preferably butyl acrylate, n-hexyl acrylate, n-octyl acrylate and 2-ethylhexyl acrylate.

12. A method according to any of claims 1 to 11 wherein the matrix of the polymer particles is formed from 25-75 weight %, preferably 35-65 weight %, most preferably 50 weight % styrene and 25-75 weight %, preferably 35-65 weight %, most preferably 50 weight % 2-ethylhexyl acrylate.

13. A method according to any of claims 1 to 12 wherein the polymer particles are formed from a monomer blend comprising cross linking monomer.

14. A method according to any of claims 1 to 13 wherein the polymer particles have a minimum film forming temperature of between -5 and 55°C, preferably between 25 and 45°C, most preferably about 35°C.

15. A method according to any of claims 1 to 14 wherein the polymer particles have a particle size in the range 80-200nm, preferably 100-120nm.

16. A method according to any of claims 1 to 15 wherein the composition (A) comprises 0.5 to 10 weight %, preferably 2.5 to 5 weight %, polymer particles and 90 to 99.5 weight %, preferably 95 to 97.5 weight %, starch based on total dry weight of polymer particles and starch.

17. A method of improving printability of a sheet of paper by applying to the surface of the formed paper sheet a composition comprising an oligomer formed from a monomer blend comprising,

(a) (meth)acrylamide,

(b) an organic mercaptan or organic sulphone,

(c) an ethylenically unsaturated monomer comprising either a tertiary amine group or a quaternary ammonium group, and

(d) optionally other monomers.

18. A method according to claim 17 wherein the composition comprises an aqueous dispersion of polymeric particles of particle size up to 1 micron, preferably 80-200nm, wherein the polymeric particles comprise a water insoluble polymer matrix, preferably formed from styrene and 2-ethylhexyl acrylate, and the oligomer is located at the surface of the polymer partcles.

19. A method according to claim 17 or claim 18 wherein the oligomer is formed from a monomer blend comprising,

(a) 85-95 mole % (meth)acrylamide,

(b) 2.5-10 mole % of an organic mercaptan or an organic sulphone, preferably dodecyl mercaptan or dodecyl sulphone,

(c) 2.5-10 mole % of an ethylenically unsaturated monomer comprising either a tertiary amine group or a quaternary ammonium group, preferably dimethylaminoethylmethacrylate, and

(d) 0-10 mole% other ethylenically unsaturated monomers, preferably acrylic acid or maleic anhydride.

20. A method according to any of claims 17 to 19 wherein the composition comprises 0.5 to 10 weight %, preferably 2.5 to 5 weight %, polymer particles and 90 to 99.5 weight %, preferably 95 to 97.5 weight %, starch based on total dry weight of polymer particles and starch.

21. A method according to any of claims 17 to 20 wherein the composition comprises optical brightening aids.

22. A composition comprising an aqueous dispersion of polymeric particles of particle size up to 1 micron, wherein the polymeric particles comprise a water insoluble polymer matrix, preferably formed from styrene and 2-ethylhexyl acrylate, characterised in that an oligomer formed from a monomer blend comprising,

(a) 85-95 mole % (meth)acrylamide and

(b) 2.5-10 mole % of an organic mercaptan or an organic sulphone, and

Sub a3

(c) 2.5-10 mole % of an ethylenically unsaturated monomer comprising either a tertiary amine group or a quaternary ammonium group, and

(d) 0-10 mole% other ethylenically unsaturated monomers, preferably acrylic acid or maleic anhydride,

is located at the surface of the polymer particles.

23. A composition according to claim 22, wherein the polymeric particles have a particle size of 80-200 nm.

Sub a4

24. A composition according to claim 22 or claim 23, wherein component (b) is dodecyl mercaptan or dodecyl sulphone, present in an amount of 2.5-5 mole % based on total oligomer.

25. A composition according to any of claims 22 to 24, wherein component (c) is dimethylaminoethyl methacrylate, present in an amount of 2.5-5 mole % based on total oligomer.

26. A composition according to any of claims 22 to 25, wherein component (d) is acrylic acid or maleic anhydride, present in an amount of 2.5-5 mole % based on total oligomer.